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(56) A process for cracking an olefin-rich hydrocarbon feedstock

(57) A process for cracking an olefin-rich hydrocarbon feedstock which is selective towards light olefins in the effluent, the process comprising passing a hydrocarbon feedstock containing one or more olefins through a moving bed reactor containing a crystalline silicate catalyst selected from an MFI-type crystalline silicate having a silicon/aluminum atomic ratio of at least 150 and an MFI-type crystalline silicate having a silicon/aluminum atomic ratio of from 150 to 200 which have been subjected to a steaming step, at an outlet temperature of from 500 to 800°C, at an olefin partial pressure of from 0.1 to 2 bars and the feedstock being passed over the catalyst at an LHSV of from 5 to 30 h⁻¹

to produce an effluent with an olefin content of lower molecular weight than that of the feedstock, intermittently removing a first fraction of the catalyst from the moving bed reactor, regenerating the first fraction of the catalyst in a regenerator and intermittently feeding into the moving bed reactor a second fraction of the catalyst which has been regenerated in the regenerator, the catalyst regeneration rate being controlled whereby the propylene purity is maintained constant at a value corresponding to the average value observed in a fixed bed reactor using the same feedstock, catalyst and cracking conditions, for example at least 60 wt%.

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Description

[0001] The present invention relates to a process for cracking an olefin-rich hydrocarbon feedstock which is selective towards light olefins in the effluent, in particular, olefin feedstocks from refineries or petrochemical plants can be cracked selectively so as to redistribute the olefin content of the feedstock to the resultant effluent.

[0002] It is known in the art to use zeolites to convert long chain paraffins into lighter products, for example in the catalytic de waxing of petroleum feedstocks. While it is not the objective of de waxing, at least parts of the paraffinic hydrocarbons are converted into olefins. It is known in the art processes to use crystalline silicates for example of the MFI or MEL type, the three-letter designations "MFI" and "MEL" each representing a particular crystalline silicate structure type as established by the Structure Commission of the International Zeolite Association. Examples of a crystalline silicate of the MFI type are the synthetic zeolites ZSM-5 and silicalite and other MFI type crystalline silicates are known in the art. An example of a crystalline silicate of the MEL type is the synthetic zeolite ZSM-11.

[0003] EP-A-0305700 discloses the production of gaseous olefins by catalytic conversion of hydrocarbons. EP-B-0347102 discloses a process for the conversion of a hydrocarbonaceous feedstock into light olefins. WO-A 96/1389 discloses a process for the conversion of C_2 - C_{12} paraffinic hydrocarbons to petrochemical feedstocks, in particular to C_2 to C_4 olefins. US-A-5068325 and EP-A-0568345 disclose the production of olefins from paraffins having four or more carbon atoms. EP-A-0511013 discloses the production of olefins from hydrocarbons using a steam activated catalyst containing phosporous and H-ZSM-5. US-A-5010052 discloses a process for the treatment of gas oils by de waxing over a silicalite catalyst. GB-A-2152045 discloses the production of isopentylene from propylene or a mixture of hydrocarbons containing propylene. GB-A-2158877 discloses the production of a isopentylene by the catalytic cracking of light distillates.

[0004] It is known in the art that for the crystalline silicates exemplified above, long chain paraffins tend to crack at a much higher rate than the corresponding long chain paraffins.

[0005] It is further known that when crystalline silicates are employed as catalysts for the conversion of paraffins into olefins, such conversion is not cyclic against time. The conversion rate decreases as the time on stream increases, which is due to formation of coke (carbon) which is deposited on the catalyst.

[0006] These known processes are employed to crack heavy paraffinic molecules into lighter molecules, however, when it is needed to produce propylene, not only are the yields low but also the stability of the crystalline silicate catalyst is low. For example, in an FCC unit a typical propylene output is 2.5wt%, the propylene output may be increased to up to about 7.5wt% propylene from the FCC unit by introducing the known ZSM-5 catalyst into the FCC unit to "equilibrate" out more propylene from the incoming hydrocarbon feedstock being cracked. Not only is this increase in yield quite small, but also the ZSM-5 catalyst has low stability in the FCC unit.

[0007] There is an increasing demand for propylene in particular for the manufacture of polypropylene.

[0008] The petrochemical industry is presently facing a major squeeze in propylene availability as a result of the growth in propylene derivatives, especially polypropylene. Traditional methods to increase propylene production are not entirely satisfactory. For example, additional naphtha steam cracking units which produce about twice as much ethylene as propylene are an expensive way to yield propylene since the feedstock is valuable and the capital investment is very high. Naphtha is in competition as a feedstock for steam crackers because it is a feed for the production of gasoline in the refinery. Propane dehydrogenation gives a high yield of propylene but the feedstock (propane) is only cost effective during limited periods of the year, making the process expensive and limiting the production of propylene. Propylene is obtained from FCC units but at a relatively low yield and increasing the yield has proven to be expensive and limited. For example methods known as metathesis or olefin metathesis enables the production of propylene from ethylene and butene, when combined with a olefin cracker, this technology is expensive since it uses ethylene as a feedstock which is at least as valuable as propylene.

[0009] Thus there is a need for a high yield propylene production method which can readily be integrated into a refinery or petrochemical plant, taking advantage of feedstocks that are less valuable for the market place (having low differentials on the market).

[0010] EP-A-0591174 in the name of Huls Aktiengesellschaft discloses the production of olefins by catalytic cracking of an olefin-rich hydrocarbon feedstock which is selective towards light olefins in the effluent. While it is disclosed that the catalyst has good stability, i.e. high activity over time, and a stable olefin conversion and a stable product distribution over time, nevertheless the catalyst stability still requires improvement, particularly when higher inlet temperatures within the liquid range disclosed (500 to 600°C) are employed in conjunction with a single reactor. That specification contemplates the use of a fixed bed reactor, although it is disclosed that a moving bed reactor, of the continuous catalytic reforming type, or a fluidized bed reactor may be employed for the olefin cracking process.

[0011] During hydrocarbon conversion reactions, a carbonaceous material, i.e. coke, can be formed and deposited on a catalyst thereby causing a loss in activity. The deposited carbonaceous material on the catalyst affects the amount of active catalyst centres on the catalyst and thereby influences the extent of the hydrocarbon conversion reaction, and hence the conversion to desired products and by-products. The presence of carbonaceous material on the catalyst

where that of the feedstock. Intermittently removing a first fraction of the catalyst from the moving bed reactor, regenerating the first fraction of the catalyst in a regenerator and intermittently loading into the moving bed reactor a second fraction of the catalyst which has been regenerated in the regenerator, the catalyst regeneration rate being controlled whereby all of the catalyst in the moving bed reactor is regenerated in a period of from 20 to 240 hours.

[0021] Preferably, the regeneration rate is controlled whereby the propylene purity is maintained constant at a value corresponding to the average value obtained in a fixed bed reactor using the same feedstock, catalyst and cracking conditions, for example at least 94 wt%.

[0022] More preferably, the regeneration rate is controlled whereby the ethylene yield on an olefin basis is less than 10 wt%.

[0023] The process invention still further provides the use of catalyst regeneration of a moving bed reactor in the catalytic cracking of an olefin containing feedstock which is selective towards lighter olefins, the catalyst regeneration being employed to average out propylene purity to higher values observed in a fixed bed reactor during an initial period, typically from 10 to 40 hours, of the olefin cracking process.

[0024] Preferably, the catalyst regeneration is also employed to average out the high ethylene yield during the initial period and the low ethylene yield during the final period observed in a fixed bed reactor.

[0025] The feedstock having at least C_4 hydrocarbons may be an effluent from a fluidised bed catalytic cracking (FCC) unit or an oil refinery.

[0026] The present invention provides a solution to the problem of loss of stability of the catalyst by the addition of the steps of removing deactivated catalyst from, and feeding reactivated catalyst into, the catalytic conversion zone which compensates for loss of activity without raising the reaction temperature. In particular, by using a moving bed reactor in which the catalyst circulates between a catalytic conversion zone and a catalyst regeneration zone. A moving bed reactor/regeneration combination still provides the possibility to operate this reaction section and regeneration section independently so they are physically isolated by means of lock hoppers and valves between the different sections. Each section can thus operate at its own optimal conditions and moreover the regeneration section can be concurrently shut down while the reaction section continues to operate.

[0027] When employing a moving bed reactor in which intermittently catalyst is withdrawn and regenerated and consequently reloaded into the catalytic reaction zone, the catalytic performance of the catalyst in the catalytic reaction zone is not undisturbed. This will result in a constant product distribution over time. Moreover, the less desired product formation, observed at the start of the catalytic cycle in fixed bed reactors, can thus be minimised because the catalytic performance in a moving bed reactor is on average at the catalytic performance observed in fixed bed reactors.

[0028] The present invention is predicated on the discovery by the inventor that in order to achieve a propylene purity i.e. a proportion of propylene in the total C_3 content of the effluent, of at least 94 wt%, and preferably also to achieve an ethylene yield on an olefin basis below 10 wt%, then the use of a moving bed reactor with catalyst regeneration enables these average values to be achieved on a continuous basis, more particularly by regulating the catalyst regeneration according to the desired propylene purity, and optimally depending on the ethylene content, which is dependent upon the particular commercial requirements for the proportion of water in the effluent, whereby the entire catalyst content of the moving bed reactor is regenerated in a period of from 20 to 240 hours. This particular period value which the entire body of catalyst in the moving bed reactor is regenerated depends on a number of factors, including the nature of the particular catalyst, temperature, FCC feedstock content, etc. Fundamentally, the catalyst regeneration is carried out so that the average values of propylene purity, and preferably also ethylene yield on an olefin basis, are such as to ensure high purity propylene is produced, with the averaging essentially overcoming the technical problem of low propylene purity and optimally high ethylene yield in a fixed bed reactor during the initial period of a fixed bed reactor, typically up to the first 10 to 30 or 20 or 40 hours, of the olefin cracking process. This overcomes the technical problem present in the prior art, in particular in EP-A-0923179, of low propylene purity, and optimally also high ethylene yield on an olefin basis, reducing the ability of the catalyst to produce acetylenichromat grade purity propylene, and optimally low ethylene content, over acceptable run times.

[0029] The preferred embodiment of the present invention can thus provide a process using a catalyst for the production of a catalytic reactor effluent characterised by a constant composition by utilising a moving bed reactor in which the catalyst circulates between a catalytic conversion zone and a catalyst regeneration zone. The preferred embodiments of the present invention can also provide a process using a catalyst whereby the formation of less desired products over fixed catalyst is quenched to an average acceptable level by utilising a moving bed reactor in which the catalyst circulates between a catalytic conversion zone and a catalyst regeneration zone.

[0030] The present invention can thus provide a process whereby olefin-rich hydrocarbon effluents (produced from refinery and petrochemical plants) are selectively cracked not only into light olefins, but particularly into propylene. In one embodiment, the olefin-rich feedstock is passed over an FCC type crystalline olefin catalyst with a particular Si to Al atomic ratio of either at least 100 obtained after water-soluble-silica elimination treatment or at least 500 with the catalyst having been prepared by crystallisation using an organic ligand and having been unsubjected to any subsequent

consisting of de-alumination process. In another embodiment, the zeolite-rich feedstock is passed over an MFI-type crystalline silicate catalyst, with a pretreated SiAl zeolite also and which has been steamed for example at a temperature of at least 400°C, for a period of at least 1 hour with a water partial pressure of at least 10 MPa. The feedstock may be passed over the catalyst at a temperature ranging between 500 to 600°C, an olefin partial pressure of from 0.1 to 2 bars and at a PHSV of from 5 to 30 bar. This can yield at least 80 to 95% propylene based on the olefin content in the feedstock, with a selectivity to propylene for the C_3 species propylene and propene (i.e. C_3/C_3 ratio) of at least 90% by weight.

[0031] In this specification, the term "olefin/alkene-rich olefin" is intended to mean the C_3/C_3 olefin ratio of the olefin feedstock which may be determined by elemental analysis. In particular, for crystalline silicate frameworks, the stated C_3/C_3 ratio refers not just to the SiAl framework of the crystalline silicate but rather to the whole material.

[0032] The feedstock may be fed either undiluted or diluted with an inert gas such as nitrogen. In the latter case, the reaction pressure of the feedstock compensates the partial pressure of the hydrocarbon feedstock in the inert gas.

[0033] In accordance with the present invention, cracking of olefins is performed in the sense that olefins in a hydrocarbon stream are cracked into lighter olefins and selectively into propylene. The feedstock and effluent preferably have substantially the same olefin content by weight. Typically, the olefin content of the effluent is within $\pm 20\%$, more preferably $\pm 10\%$, of the olefin content of the feedstock. The feedstock may comprise any kind of olefin containing hydrocarbon stream. The feedstock may typically comprise from 1% to 100% olefin and furthermore may be fed undiluted or diluted by a diluent, the diluent optionally including a non-olefin hydrocarbon. In particular, the olefin-containing feedstock may be a hydrocarbon stream containing normal and branched olefins in the carbon range C_2 to C_{10} , more preferably in the carbon range C_2 to C_6 , optionally in a mixture with normal and branched paraffins and/or aromatics in the carbon range C_2 to C_{10} . Typically, the olefin-containing stream has a boiling point of from about 15 to 200°C.

[0034] In particularly preferred embodiments of the present invention, the hydrocarbon feedstock comprises C_4 and/or C_5 paraffins and/or olefins and/or aromatic units. Such olefin cracking units crack a wide variety of feedstocks, including ethane, propane, butane, pentane, gas oil, fuel oil, etc. Most particularly, the hydrocarbon feedstock may comprise a C_4 cut from a fluidized bed catalytic cracking (FCC) unit or a crude oil refinery which is employed for converting heavy oil into gasoline and lighter products. Typically, such a C_4 cut from an FCC unit comprises around 50wt% olefin. Alternatively, the hydrocarbon feedstock may comprise a C_4 cut from a light naphtha crude oil refinery for producing naphtha reformer effluent (NREF) which is prepared from naphthalene and isobutane. Again, such a C_4 cut from the NREF unit typically comprises around 60wt% olefin. These C_4 cuts are fractionated at the outlet of the respective FCC or NREF unit. The hydrocarbon feedstock may yet further comprise a C_4 cut from a naphtha desulfurization unit or a petrochemical plant in which naphtha, comprising C_4 to C_{10} species having a boiling point range of from about 10 to 150°C, is steam cracked to produce, *inter alia*, a C_4 cut. Such a C_4 cut typically comprises, by weight, 40 to 50% 1,3-butadiene, around 25% isobutylene, around 15% butene in the form of sub-1-type and/or tri-1-ene and around 10% isobutene and/or isobutane. The olefin-containing hydrocarbon feedstock may also comprise a C_4 cut from a steam cracking unit, after butadiene extraction (Hartman 1), or after butadiene hydrogenation.

[0035] In accordance with the present invention, the catalyst for the cracking of the olefin comprises a crystalline silicate of the MFI family which may be a zeolite, a silsesquioxane or any other silicate in this family or the MFI family which may be a zeolite or any other silicate in that family. Examples of MFI silicates are ZSM-5 and silsesquioxane. An example of an MFI zeolite is ZSM-5 which is known in the art. Other examples are Garatite II, and silsesquioxane as described by the International Zeolite Association (Bae of zeolite nomenclature, 1997, Bitterwolf et al.).

[0036] The zeolite/crystalline silicates have pores or channels defined by tetrahedral rings and a high olefin/alkene-rich olefin ratio.

[0037] Crystalline silicates are microcrystalline crystalline ligands polymers based on a framework of SiO_4 tetrahedra linked by each other by sharing of oxygen ions, where X may be trivalent (e.g. Al, Ga, \dots) or tetravalent (e.g. Si, Ti, \dots). The crystal structure of a crystalline silicate is defined by the specific order in which a network of tetrahedral units are linked together. The size of the crystalline silicate pore openings is determined by the number of tetrahedral units, or, alternatively, oxygen atoms, required to form the pores and the nature of the cations that are present in the pores. They possess a unique combination of the following properties: high internal surface area; uniform pores with one or two discrete sizes; low mechanical stability; good thermal stability; and ability to accept organic compounds. Since the pores of these crystalline silicates are stable in size to many organic molecules of various interest, they tend to be sieved and access to reactants and products, resulting in parallel selectivity in catalytic reactions. Crystalline silicates with the MFI structure possess a 3D-disordered hexagonal pore system with the following pore diameters: straight channels along [100]: 0.55 to 0.60 nm and a sinusoidal channel along [110]: 0.51 to 0.56 nm. Crystalline silicates with the MFI structure possess a 3D-directional intersecting straight pore system with straight channels along [110] having pore diameters of 0.55 to 0.60 nm.

[0038] The crystalline silicate catalyst has structural and chemical properties and is employed under particular reaction conditions whereby the catalytic cracking readily proceeds. Different reaction pathways can occur on the catalyst.

under one process conditions, having an inlet temperature of around 500 to 600°C, preferably from 520 to 580°C, yet more preferably 540 to 560°C, and an outlet total pressure of about 0.1 to 2 bars, most preferably around atmospheric pressure, the shift of the double bond of an olefin in the feedstock is readily minimized, leading in double bond isomerization. Furthermore, with one process it is possible to achieve thermodynamic equilibrium. Propylene can be, for example, directly produced by catalytic cracking of hexane or a heavier olefin feedstock. Olefin catalytic cracking may be understood to comprise a process yielding stream mixtures, via bond cleavage.

[0039] With such high silica/aluminum ratio in the crystalline silica catalyst, a stable yield distribution can be achieved with a high propylene yield of an olefin feed of from 20 to 50% whatever the origin and composition of the olefin feedstock. Such high yields require the stability of the catalyst, thereby increasing the stability of the catalyst.

[0040] The MFI catalyst having a high silica/aluminum atomic ratio for use in the catalytic cracking process of the present invention may be manufactured by removing aluminum from a commercially available crystalline silicate. A typical commercially available silicate has a silica/aluminum atomic ratio of about 120. The commercially available MFI crystalline silicate may be modified by a sintering process which reduces the interstitial aluminum in the crystalline silicate framework and converts the aluminum atoms into octahedral aluminum in the form of amorphous alumina. Although in the sintering step aluminum atoms are theoretically removed from the crystalline silicate framework structure in form of amorphous alumina, these particles cause partial obstruction of the pores or channels in the framework. This inhibits the olefin cracking processes of hydrogen transfer. Accordingly, following the sintering step, the crystalline silicate is subjected to an extraction step wherein amorphous alumina is removed from the pores and the mesopore system by the formation of a water-soluble aluminum complex via the overall effect of de-alumination of the MFI crystalline silicate. In this way by removing aluminum from the MFI crystalline silicate framework and then extracting amorphous alumina formed therefrom from the pores, the process of producing a substantially homogeneous de-alumination throughout the whole pore surfaces of the catalyst. This reduces the acidity of the catalyst, and thereby reduces the occurrence of hydrogen transfer reactions in the cracking process. The reduction of acidity thereby produces substantially homogeneously throughout the pores defined in the crystalline silica framework. This is because in the cracking process hydrocarbon molecules enter deeply into the pores. Accordingly, the reduction of acidity and thus de-alumination in hydrogen transfer reactions which would reduce the stability of the MFI catalyst are reduced throughout the whole pore structure in the framework. The remaining silica/aluminum ratio may be increased by this process to a value of at least about 180, preferably from about 180 to 1000, more preferably at least 200, yet more preferably at least 300, and most preferably around 400.

[0041] The MFI, or MFI crystalline silica catalyst may be mixed with a binder, preferably an inorganic binder, and shaped to a desired shape, e.g. extruded pellet. The binder is selected so as to be resistant in the isoprenol and other conditions employed in the catalyst manufacturing process and in the subsequent catalytic cracking process for the olefin. The binder is an inorganic material selected from clays, silica, metal oxides such as ZrO₂ and/or metal, or salts including various silicates and metal oxides. The binder is preferably alumina-free. Although aluminum in certain chemical compounds such as AlPO₄ may be used as the binder as a pore-former and not acidic in nature, if the binder when it is used in conjunction with the crystalline silicate is itself catalytically active, this may alter the character of the selectivity of the catalyst. Inactive materials for the binder may suitably serve as diluents to control the amount of conversion so that products can be obtained monotonically and orderly without employing other means for controlling the reaction rate. It is desirable to provide a catalyst having a good crush strength. This is because in commercial use, it is desirable to prevent the catalyst from breaking down into interstitial materials. Such clay or oxide binders have been employed normally only for the purpose of improving the crush strength of the catalyst. A particularly preferred binder for the catalyst of the present invention comprises silica.

[0042] The relative proportions of the finely divided crystalline silica material and the inorganic binder portion of the binder can vary widely. Typically, the binder content ranges from 5 to 10% by weight, more typically from 20 to 30% by weight, based on the weight of the nonpore catalyst. Such a mixture of crystalline silica and an inorganic oxide binder is referred to as a formulated crystalline silicate.

[0043] In mixing the catalyst with a binder, the catalyst may be formulated into pellets, spheres, extrudates into other shapes, or formed into a spray-dried powder. For producing the present invention it is preferred that the formulated catalyst has a very symmetrical shape like a sphere and pellets or extrudates having equal height and widthness. It is important that the settling velocity of the catalyst particles in a gas stream is the same for all orientations relative to the gas stream direction.

[0044] In the catalyst cracking process, the process conditions are selected in order to provide high selectivity to, where propylene, a stable olefin composition over time, and a stable yield distribution in the effluent. Such objectives are favoured by the use of a low acid density in the catalyst, i.e. a high Si/Al atomic ratio in conjunction with a low pressure, a high inlet temperature and a short contact time, all of which process parameters are interrelated and provide an overall catalytic effect (e.g. lighter reactions may be offset or compensated by a relatively higher temperature). The process conditions are selected to achieve high hydrogen transfer reactions leading to the formation

of paraffins, aromatics and coke derivatives. The process operating conditions thus employ a high space velocity, a low pressure and a high reaction temperature. The catalyst ranges from 5 to 500 g/l, preferably from 10 to 200 g/l. The olefin partial pressure ranges from 0.1 to 2 bars, preferably from 0.5 to 1.5 bars. A particularly preferred olefin partial pressure is atmospheric pressure (i.e. 1 bar). The hydrocarbon feedstocks are preferably fed at a total inlet pressure sufficient to convey the feedstocks through the reactor. The two-carbon feedstocks may be fed undistilled or distilled in an inert gas, e.g. nitrogen. Preferably, the total absolute pressure in the reactor ranges from 0.5 to 10 bars. The use of a low inlet partial pressure, for example atmospheric pressure, tends to lower the incidence of hydrogen transfer reactions in the cracking process, which in turn reduces the potential for coke formation which tends to reduce catalyst stability. The cracking of the olefin is preferably performed at an inlet temperature of the feedstock of from 500 to 600°C, more preferably from 550 to 580°C, yet more preferably from 540 to 580°C, typically around 560°C to 565°C. Embodiments of the present invention will now be described, by way of exemplification, with reference to the accompanying drawings, in which:

Figure 1 is a schematic process scheme in accordance with one embodiment of the present invention for processing refinery and/or petrochemical feedstocks, the process scheme incorporating a process for selectively catalytically cracking olefins into lighter olefins over a crystalline silicate catalyst and incorporating catalyst regeneration;

Figure 2 shows a schematic process scheme in accordance with a second embodiment of the present invention for processing refinery and/or petrochemical feedstocks, the process scheme incorporating a process for selectively catalytically cracking olefins into lighter olefins over a crystalline silicate catalyst and catalyst regeneration;

Figure 3 shows a schematic process scheme in accordance with a third embodiment of the present invention for processing refinery and/or petrochemical feedstocks, the process scheme incorporating a process for selectively catalytically cracking olefins into lighter olefins over a crystalline silicate catalyst and catalyst regeneration;

Figure 4 shows the relationship between the olefin content of an effluent and time for an example of a catalytic cracking process; and

Figure 5 shows the relationship between olefin content and time for a second example of a catalytic cracking process.

Figure 6 provides a schematic illustration of a configuration for cracking the paraffins of the present invention. The description is not intended to require certain configurations and in order to simplify the drawing, not all valves, control flow controlling valves, sensors, piping and other conventional equipment readily known by the person skilled in the art are not shown.

[0046] The paraffin-rich reacting feed may be catalytically cracked and preferably combined with recycle feed, and optionally a diluting gas like hydrogen, steam or any other inert gas, and sent through line 1 to a first-effluent heat exchanger 2 and further through line 3 to a heater 4 to raise the temperature of the mixture to the desired reaction temperature. Through line 5 the hot mixture is sent into a reaction reactor 10. The reactor 10 contains an amount of dehydrogenation catalyst. The feed mixture may be injected in the centre of the annulus and may leave the catalyst external to the catalyst bed annulus. Alternatively, the feed mixture may be injected in the catalyst bed external to the bed annulus and may leave the catalyst bed annulus in the centre of the annulus. The reaction products leave the reaction section through line 12 via the first-effluent heat exchanger 2 to the fractionation section not shown. In the fractionation section the different reaction products are separated. Unreacted feed or a preformed olefin-rich C₂ fraction may be recycled together with fresh feed to the reaction section through line 1.

[0047] In accordance with the catalyst regeneration in the moving bed reactor in the present invention, the catalyst builds down under gravity through the catalyst bed annulus and is continuously or intermittently withdrawn through line 23 into a lock hopper 21 where the catalyst is purged with nitrogen in order to remove hydrocarbon vapours from the catalyst. In the lock hopper the pressure is controlled to that of a lift sump 22. The catalyst is lifted from the lift sump 22 by means of a lift gas conduit through line 24 to a lift dis-engager 25 through a catalyst lift line 26. The gaseous lift gas may be hydrogen, nitrogen, methanol, steam or even diluted oxygen in nitrogen. The flow rate of the lift gas is sufficient to suspend the settling velocity of the catalyst particles in order to transfer the catalyst through the lift line 24 to a lift dis-engager 25. In the lift dis-engager 25, the catalyst is separated from the lift gases through line 27 and the process is controlled to the procedure of a catalyst regeneration vessel 40. The lift gases may be recycled or sent to a flare or purge. The catalyst is fed from the lift dis-engager 25 through line 28 to the regeneration vessel 40.

[0048] In the regeneration vessel 40 the carbonaceous material laid down on the catalyst is burned off by means of oxygen, or formic acid dioxide. The regeneration vessel 40 may include a synthetic moving bed of catalyst travelling down by gravity.

[0046] Alternatively, it may also consist of a radial-flow type catalyst bed. The oxidising gases are injected at the centre of the catalyst bed annulus or from the exterior of the annulus. Fresh air is introduced through line 41, mixed with recycle gas coming through line 46 and compressed by means of a compressor 42 into line 43. The oxygen-containing oxidising gases from line 43 enter the regeneration vessel 44. The combustion gases leave the regeneration vessel through line 45 and pass to a vessel 47. The combustion gases are cooled down or heat exchanged and eventually direct water is drained off through line 48. Uncondensed gases are partially stripped out through line 47 and the remaining may be recycled and mixed with fresh air through line 41.

[0047] To control the combustion of the heterogeneous material in the catalyst the oxygen should be present at relatively low concentrations. The ratio of oxygen gas to fresh air is generally high. The molar percent of oxygen in the oxidising gas is typically from 0.2 to 2, preferably about 0.8. Other compounds may be present in the oxidising gas, such as carbon dioxide, nitrogen and carbon monoxide.

[0048] During the regeneration the catalyst beds show outer glowing and the endothermic material is progressively burned off. It may be desirable to use higher concentrations of oxygen towards the end of the regeneration vessel 44. A excess ratio of oxygen containing gas may be injected into the regeneration vessel 44 near to the lower part of the catalyst bed where carbonaceous material is already burned off by a gas stream. As is known, regeneration with oxygen is exothermic and care should be taken not to exceed the temperatures at which the catalyst is damaged. It is preferred not to surpass 600°C in the catalyst bed. The regeneration is generally completed about 450°C. Therefore the oxygen-containing gas may be heated up before entering the regeneration vessel 44. The excess oxygen containing stream which may be injected into the regeneration vessel may be heated up to a higher temperature by which better the burn off of carbonaceous materials laid down on the catalyst. The molar percent of oxygen in the excess oxygen-containing stream is typically from 0 to 100, preferably from 5 to 1. Other compounds may be present in the oxidising gas, such as carbon dioxide, nitrogen and carbon monoxide.

[0049] The catalyst flows through line 50 to a hopper 51. Optionally, the regeneration may be finished first by purging first the hopper 51 with pure air at the highest allowable temperature for the catalyst, followed by a nitrogen purge in order to remove any remaining oxygen. The catalyst further flows through line 52 to a lift hopper 52. By means of a lift gas coming through line 54, the catalyst is sent to a catalyst collector hopper 53 where it is sent to the reactor 10 through a catalyst transfer line 55. The catalyst is separated from the lift gases through line 56. These lift gases may be sent to other purposes or may be recycled and used again as lift gas. The pressure in the catalyst collector hopper 53 is adjusted to the reactor pressure. The regenerated catalyst in the collector hopper 53 flows through line 58 into the reactor vessel 10. Flow back catalyst may be added via the catalyst collector hopper 53 through line 59, while used catalyst can be withdrawn from the regeneration system through line 60.

[0050] Figure 2 shows an alternative arrangement for providing the catalyst invention. As the cracking of long-chain alkanes into lighter alkanes is an endothermic reaction, it may be desirable to provide the reaction system. Figure 2 shows the alternative embodiment with two reacting reactors 10, 15 in series for the olefin cracking process. The reactor effluent of the first reactor flow reactor 10 leaves the reactor through line 11 and is sent to a reactor 15. The mixture is sent through line 13 into the second reactor 15. The second reactor 15 may be identical to the first reactor 10 as illustrated or optionally the second reactor 15 is parallel to the first reactor 10. In the latter case, there is provided a catalyst lift transfer line that allows bypassing the first and the second reactors 10, 15. The rest of the process scheme is the identical shown for Figure 1. As the catalyst becomes less active when cycling down through the cracking bed, it may be desired to increase the thickness of the reaction mixture with the catalyst in the second reactor. This can easily be done by increasing the thickness of the catalyst bed therein.

[0051] A further embodiment for providing the present invention is shown in Figure 3. As the reactors are not very large, it can be advantageous to place the regeneration vessel 44 on top of the first reactor 10 for one single reactor 10 as shown in Figure 3. This implies only lower catalyst transfer line which will reduce the drying of the catalyst during the transport step.

[0052] The present invention will now be described with reference to the following non-limiting examples.

EXAMPLE 1

[0053] A feedstock having the feed composition shown in Table 1, consisting of a 50/50 wt% mixture of C₁₂s and C₁₆s, subjected to net FCC unit was subjected to olefin catalytic cracking in a fixed bed reactor that in accordance with the invention comprising a catalytic waste catalyst of the SF₆ type (as generally disclosed in EP-A-0821173) having a deactivation/deactivation ratio of at least 27% at an inlet temperature of 525°C, a inlet molar excess oxidizing (O₂) of 20% and an inlet pressure of 1.5 bars. The composition of the olefin overhead was measured by determining the propylene (C₃) content, the ethylene (C₂) content, the butylene (C₄) content and the propylene purity and the results are shown in Figure 4. The reactor is loaded with a layer of catalyst and the reactor operates in an adiabatic mode.

[0054] From Figure 4 it may be seen that the propylene content, i.e. the yield on a molar basis towards propylene

of the olefin cracking process is initially slightly greater than or about 25 wt% up to a period of around 25 hours, after which the propylene content usually decreases to a value of as low as about 10 wt% after a period of about 25 hours. This shows that the activity of the catalyst towards the production of propylene in the olefin cracking process increases considerably, specifically for runs greater than around 25 hours. In addition, for shorter reaction times in stream, there are features in that the ethylene content of an olefin-based effluent is usually high, starting from greater than 10 wt% and being greater than 15 wt% up to 40 hours on stream, whereas the propylene purity (i.e. the ratio of propylene to total C₃ content) is initially low and increases to a value greater than 54 wt% only after a period of around 40 hours on stream.

Table 2 shows values of the propylene content, ethylene content, isobutene content and propylene purity after a specific time on stream, up to about 25 hours on stream, during which the propylene yield is quite consistent.

In accordance with the process of the present invention, by providing a moving bed reactor with continuous catalyst regeneration, the four discrete yields in the effluent are automatically averaged to yield the average values also specified in Table 2. It may thus be seen that by using a moving bed reactor in conjunction with continuous catalyst regeneration, the composition of the effluent may be made more constant. In particular the propylene content and purity. Moreover, the formation of less desired products in the effluent, such as ethylene, which requires a relatively difficult fractionation process to be separated from the desired propylene, is reduced considerably to an average level as compared to the initial level in the case of a fixed bed.

EXAMPLE 2

In accordance with this Example, the same bed having a typical composition illustrated in Table 1 was fed over the same catalyst as in Example 1 and at the same inlet temperature and outlet pressure but at a lower LHSV of 10/h. The relationship between the olefin content and time on stream is illustrated in Figure 5. Table 5 shows the variation between the propylene, ethylene and isobutene contents with time, together with the propylene purity variation with time.

As for Example 1, in Example 2 it may be seen that the use of a moving bed reactor together with catalyst regeneration provides a substantially average value for the composition of the effluent which tends to provide set improved average values for the ethylene content and an improved average value for the propylene purity.

TABLE 5

FEED COMPOSITION (WT%)						
C ₄ or	P	E	N	I	Total	Cumulative
1					0.00	
2					0.00	1.00
3	0.02	0.20			0.22	1.22
4	17.40	25.74			43.14	44.36
5	0.02	0.20	0.29		13.13	57.49
6	0.02	1.54	1.50	0.32	13.48	70.96
7	0.90	0.10	2.59	0.00	13.60	84.56
8	0.22	1.42	2.10	0.26	13.28	97.84
9	1.20	0.20	0.14	1.06	3.72	98.40
10	0.14	0.08	0.00	0.40	0.62	98.97
11				0.03	0.10	100.00
Total	45.10	42.37	5.23	0.70	100.00	

TABLE 7

EXAMPLE 1				
PROP%	4.17	11.46	34.27	AVERAGE
C ₂ (wt%)	37.77	36.65	25.14	36.50

TABLE 2 (continued)

EXAMPLE 1				
CO ₂ (wt%)	17.68	7.18	6.35	7.88
H ₂ O (wt%)	18.58	18.46	22.90	18.25
CO ₂ -free (wt%)	66.74	94.93	96.46	92.91

TABLE 3

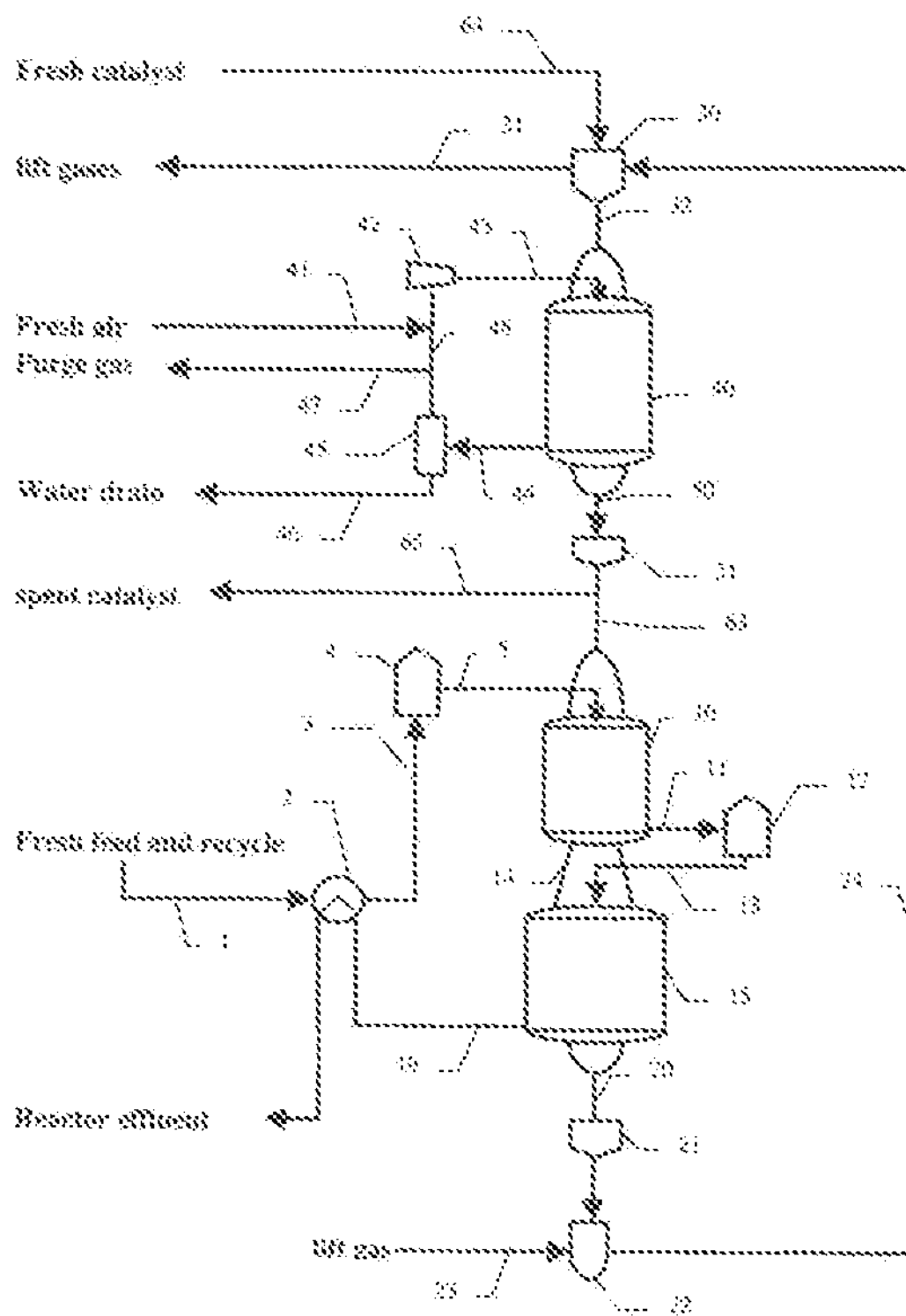
EXAMPLE 2							
YDSR (%)	2.47	4.36	10.18	17.87	28.57	41.10	AVERAGE
CO ₂ (wt%)	32.68	35.74	23.81	30.49	36.86	38.09	32.83
CO ₂ (wt%)	10.88	10.71	9.93	8.94	6.66	7.64	9.40
H ₂ O (wt%)	14.54	11.66	12.21	12.82	14.34	15.47	13.68
CO ₂ -free (wt%)	58.58	61.42	61.70	62.18	56.64	61.47	59.09

Claims

1. A process for making an olefin containing hydrazine feedstock which is selectively towards light olefins in the effluent, the process comprising passing a hydrocarbon feedstock containing one or more olefins through a moving bed reactor maintaining a crystalline silicate catalyst selected from an MFI-type crystalline silicate having a silicon substitution atomic ratio r_1 of at least 180 and an MFI-type crystalline silicate having a silicon substitution atomic ratio r_2 from 160 to 800 which has been subjected to a deactivation step, at an inlet temperature of from 500 to 600°C, at an olefin partial pressure of from 0.1 to 2 atm and the feedstock being passed over the catalyst at an LHSV of from 0 to 300 h⁻¹ to produce an effluent with an olefin content of lower molecular weight than that of the feedstock; intermittently removing a first fraction of the catalyst from the moving bed reactor, regenerating the first fraction of the catalyst in a regenerator and intermittently burning into the moving bed reactor a second fraction of the catalyst which has been regenerated in the regenerator, the catalyst regeneration rate being controlled whereby the propylene purity is maintained constant at a value corresponding to the average value obtained in a fixed bed reactor using the same feedstock, catalyst and reacting conditions, for example at least 94 wt%.
2. A process according to claim 1, wherein the catalyst regeneration rate is controlled whereby the ethylene yield on an olefin basis is less than 10 wt%.
3. A process for making an olefin containing hydrazine feedstock which is selectively towards light olefins in the effluent, the process comprising passing a hydrocarbon feedstock containing one or more olefins through a moving bed reactor maintaining a crystalline silicate catalyst selected from an MFI-type crystalline silicate having a silicon substitution atomic ratio r_1 of at least 180 and an MFI-type crystalline silicate having a silicon substitution atomic ratio r_2 from 160 to 800 which has been subjected to a deactivation step, at an inlet temperature of from 500 to 600°C, at an olefin partial pressure of from 0.1 to 2 atm and the feedstock being passed over the catalyst at an LHSV of from 0 to 300 h⁻¹ to produce an effluent with an olefin content of lower molecular weight than that of the feedstock; intermittently removing a first fraction of the catalyst from the moving bed reactor, regenerating the first fraction of the catalyst in a regenerator and intermittently burning into the moving bed reactor a second fraction of the catalyst which has been regenerated in the regenerator, the catalyst regeneration rate being controlled whereby all of the catalyst in the moving bed reactor is regenerated in a period of from 20 to 240 hours.
4. A process according to claim 3 wherein the propylene purity is maintained constant at a value corresponding to the average value obtained in a fixed bed reactor using the same feedstock, catalyst and reacting conditions, for example at least 94 wt%.
5. A process according to claim 3 or claim 4 wherein the regeneration rate is controlled whereby the ethylene yield on an olefin basis is less than 10 wt%.

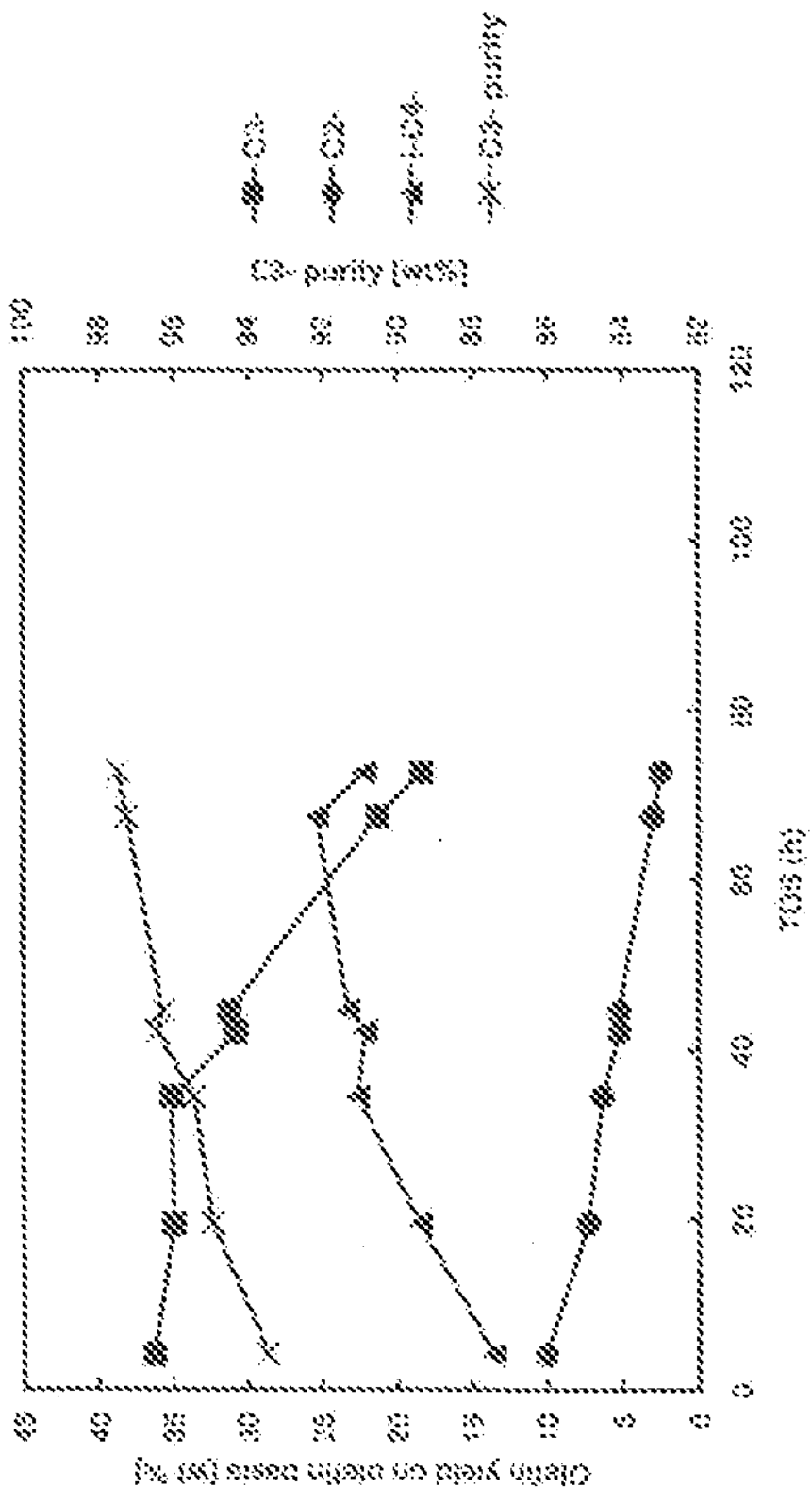
8. Use of catalyst regeneration is a moving bed reactor for the catalytic cracking of an olefin containing feedstock which is selective towards lighter olefins, the catalyst regeneration being employed to average out the catalyst activity in higher ethane conversion in sufficient reaction during an initial period of the multi-cracking process
9. Use according to claim 8 wherein the total period is from 10 to 40 hours.
10. Use according to claim 8 or claim 9 wherein the catalyst regeneration is also employed to average out the high ethylene yield during the initial period and the low ethylene yield during the final period observed in a burst test reactor.

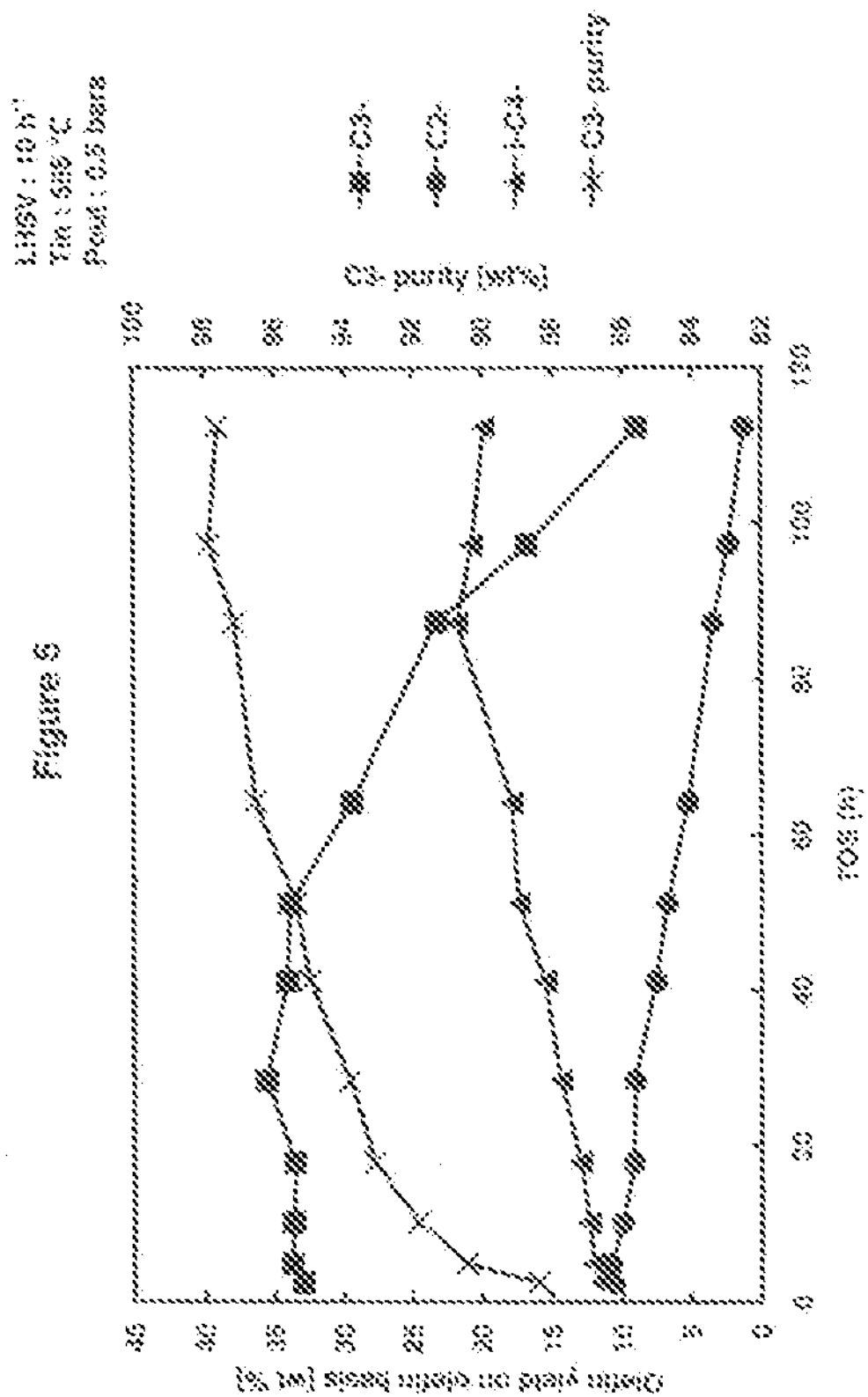
FIGURE 3



Time : 20 min
 Temp : 55°C
 Flow : 0.5 ml/min

Figure 4





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ANNEX TO THE EUROPEAN SEARCH REPORT
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The annex lists the patent family members relating to the invention described in the above-mentioned European patent application.
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